

## Critical comparison between time- and frequency-domain relaxation functions

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Considerable work has been performed on providing a theoretical basis for the Kohlrausch-Williams-Watts (KWW) and Havriliak-Negami (HN) relaxation functions. Because of this, several papers have examined the “interconnection” of these two functions. In this paper, we demonstrate that, with achievable instrumental sensitivity, these two functions are distinguishable. We further address the issue of the “universal” limiting power laws and the ability to obtain the exponents associated with them. Finally, the stability and accuracy of our numerical Laplace transform is demonstrated by comparison between functions with known analytical time and frequency solutions. The stability of our algorithm indicates that the method of Alvarez and co-workers [F. Alvarez, A. Alegría, and J. Colmenero, *Phys. Rev. B* **44**, 7306 (1991)] is an unnecessary approximation for converting between the time and frequency domain. [S0163-1829(99)01026-7]

### I. INTRODUCTION

The nature of the glass transition has plagued researchers for over a century. There are those who believe that there is a thermodynamic transition underlying the kinetically observed phenomena and there are those who feel that it is solely a dynamically based effect. One aspect of the glass transition that each model tries to explain is the nonexponential long-time relaxation behavior. An empirical expression which is frequently utilized for fitting this behavior is the Kohlrausch-Williams-Watts (KWW) function (stretched exponential)<sup>1,2</sup>

$$\Phi_{\text{KWW}}(t) = 1 - \exp\left[-\left(\frac{t}{\tau_0}\right)^k\right], \quad (1)$$

where  $\tau_0$  is a characteristic relaxation time and  $k$  is a parameter that has values ranging from 0 to 1. This equation was introduced in 1863 to describe mechanical creep in glass fibers<sup>1</sup> and many theoretical models have been developed to reproduce this equation. DiMarzio and co-workers<sup>3,4</sup> arrived at this function by postulating potential wells in phase space in which particles become trapped. The probability distribution for these wells is an exponential decay in time, but because of the distribution of varying depths of the wells, a stretched exponential is obtained. Palmer and co-workers<sup>5</sup> and Muñoz and co-workers<sup>6</sup> postulate hierarchically constrained models in which slow motions are constrained by a necessity of movement of faster motions in a particular manner. Shlesinger and co-workers base their theory on the existence of mobile defects (which are unidentified to keep the model as general as possible) that diffuse anomalously and quench localized excitations.<sup>7-13</sup> The defects in the Shlesinger model are commonly identified as “packets” of free volume. Mansfield<sup>14</sup> has developed a model of the glass transition which incorporates these defects as well. Douglas and Hubbard<sup>15</sup> proposed a semiempirical model, based on a time-translation kernel which was consistent with stretched exponential behavior, that was able to reproduce a number of the other properties of glass formers [in this model  $(1-k)$  is a measure of the material inhomogeneity]. The above have

been presented only for illustrative purposes and as such, are a small subset of the total number of models that have attempted to give a theoretical justification to the empirical KWW relationship [Eq. (1)].

In the frequency domain, the Havriliak-Negami (HN) equation<sup>16</sup>

$$\phi_{\text{HN}}(\omega) = \frac{1}{[1 + (i\omega\tau)^\alpha]^\beta}, \quad (2)$$

is often used to model relaxation phenomena. Because of this, several papers have attempted to demonstrate the “equivalence” of the Havriliak-Negami and KWW equations. Lindsey and Patterson<sup>17</sup> examined the ability of the Cole-Davidson equation [Eq. (2) with  $\alpha=1$ ] to approximate the Laplace transform of the KWW equation. They state that numerical relationships could be obtained to relate the approximation of the KWW equation to the HN equation, however they state that “Such a comparison is, of course, not exact; it is presented only to ease the comparison process, particularly between older dielectric data analyzed using the Cole-Davidson function (CD) (introduced in 1950), and the more recent Williams-Watts function (used for dielectric relaxation measurements in 1969).”<sup>17</sup> Additionally, they concluded that while the relaxation functions (CD and KWW) have similar shapes, their distribution functions have very dissimilar shapes at long times.

Alvarez, Alegría, and Colmenero<sup>18,19</sup> used a method based on a distribution of relaxation times in order to avoid what they claimed were the problems with the Fourier transform of the KWW function. They state that “Several methods have been used to Fourier transform the KWW function and to interpret relaxation data from spectroscopies in the frequency domain. However, it is also well known that computation of Fourier transform poses numerical problems originating from cutoff effects which yield unwanted oscillations, especially when treating real data.”<sup>18</sup> Alvarez and co-workers used the mean-square difference as a measure of the compatibility, or equivalence, of the HN and KWW functions. For one of their comparisons, they claim that their low value of  $1.89 \times 10^{-5}$  is very good, and state that one can

therefore assume that the two functions are “equivalent.” Empirical relationships were presented in this work which related the parameters of the KWW equation to those of the HN equation. The intent was to allow transformation between the time and frequency domain without resorting to the Laplace transform.

The statements made by Alvarez and co-workers, regarding the Fourier transform, are correct for a fast-Fourier transform. They are incorrect, however, when applied to a suitably computed numerical Laplace transform that takes account of the finite data window, which is the proper numerical method for transforming time-domain data to the frequency domain.<sup>20,21</sup> This is evident, as one of us has successfully demonstrated a numerically stable Laplace transform which can be used to transform a time-domain function (or time-domain data) to its frequency-domain equivalent within an arbitrarily chosen tolerance.<sup>21–24</sup>

Havriliak and Havriliak,<sup>25</sup> in a manner similar to Alvarez and co-workers, used statistical procedures to support the claim that, for some ranges of the  $\beta$  parameter, the KWW and HN functions are the same. They cited the confidence interval for the exponents as proof of this assertion; however, unlike Alvarez and co-workers they did not give the standard deviations of their fits. It is also stated later in their paper, in apparent contradiction to their earlier statement on confidence limits, that, because the limiting high/low-frequency behavior of the KWW function is best described by the CD function, the KWW is not universal because Jonscher’s studies<sup>26</sup> on the limiting power-law behavior suggested that these specific limiting exponents are not universal.

In a recent paper<sup>27</sup> (henceforth referred to as Paper I) we examined the question of how unique the fit parameters are between two different representations of relaxation data over limited frequency ranges. In that work, we also addressed the issue of equivalence of two functions and the proper measure of the ability of one function to approximate another. In this work, we will re-examine the ability of the HN equation to approximate the Laplace transform of the KWW function over the entire range of significant variation of the loss component of the transformed data with careful consideration of the measure we presented in Paper I. In this paper, it will be demonstrated that, with achievable instrumental sensitivity, the two functions are distinguishable, and we will point out some logical inconsistencies in the work of Alvarez and co-workers<sup>18,19</sup> and Havriliak and Havriliak.<sup>25</sup> Furthermore, we will examine the limiting power-law behavior of these functions and will show how broad a frequency range must be covered to determine this limiting behavior. From this, we can demonstrate that for a wide range of values of the KWW exponent  $k$ , empirical determination of both the low- and high-frequency power laws is very difficult.

## II. PROCEDURE

### A. Numerical Laplace transform and fitting of data

A time to frequency domain transformation is accomplished through the Laplace transform:

$$\phi(\omega) = \lim_{\text{Re}(s) \rightarrow 0^+, \text{Im}(s) = \omega} \int_0^{\infty} \exp(-st) \left[ \frac{-d\Phi(t)}{dt} \right] dt, \quad (3)$$

where  $\Phi(t)$  is the time-domain response function to a unit step excitation,  $\phi(\omega)$  is the frequency-domain response function, and  $s$  is the complex variable  $s = \nu + i\omega$ . As a response to criticisms of the numerical Laplace transform for time-domain measurements,<sup>28</sup> one of us has demonstrated the stability of the numerical Laplace transform.<sup>21–24</sup> In this paper, we will utilize the algorithm described in one of those papers<sup>24</sup> to transform our time-domain functions into the frequency domain. Since this procedure is defined in terms of a desired tolerance, we chose a tolerance of  $1 \times 10^{-6}$  or less for all of our transformed data, except for  $k=0.1$ , for which we used a tolerance of  $1 \times 10^{-7}$ . This guarantees that the transformation error was sufficiently small so as to not significantly affect any results reported in this paper. The frequency window for the transformation, setting  $\tau=1$  s, was chosen such that the loss component of frequencies above and below this window had negligible contributions to the total area as a function of  $\log_{10} \omega$ . We would like to emphasize the fact that although we generated data to a frequency as low as  $10^{-12} \text{ s}^{-1}$  we recognize that this time corresponds to an experimental time *greater than the recorded history of civilization*. These curves are generated for illustrative purposes only. Values of 0.1, 0.3, 0.5, and 0.7 were chosen for  $k$  to represent the total range of behavior of the KWW relaxation function. (Note that for  $k=1.0$ , the KWW reduces to a Debye function which has the known frequency-domain HN parameters:  $\alpha=1.0$  and  $\beta=1.0$ .) We also want to mention that in the previous paper on the Laplace transform,<sup>24</sup> it was demonstrated that the algorithm was sufficient to transform the  $k=1$  case into the Debye function with an absolute error of less than  $1 \times 10^{-6}$  over the entire range when set for a tolerance of  $1 \times 10^{-6}$ .

Two sets of curve fits to the transformed data were obtained: one to the imaginary component only (fit A) and one simultaneously to the real and imaginary components (fit B). The data were treated as if they were obtained from a time-domain dielectric spectrometer. The data obtained from the Laplace transform were in the form of the complex frequency dependent dielectric constant  $\epsilon^*(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ , where  $\epsilon'$  and  $\epsilon''$  are the real and imaginary components. Therefore, curve fits were performed to the following equation:

$$\epsilon^*(\omega) = (\epsilon_0 - \epsilon_\infty) \phi_{\text{HN}}(\omega) + \epsilon_\infty = \frac{(\epsilon_0 - \epsilon_\infty)}{[1 + (i\omega\tau)^\alpha]^\beta} + \epsilon_\infty, \quad (4)$$

where  $(\epsilon_0 - \epsilon_\infty)$  is the dispersion strength and  $\epsilon_\infty$  is the high-frequency dielectric constant. Note that after  $(\epsilon_0 - \epsilon_\infty)$ ,  $\alpha$ ,  $\beta$ , and  $\tau$ , were obtained for fit A,  $\epsilon_0$  was obtained from a linear least squares to the real component, fixing the aforementioned parameters. The fits to Eq. (4) were performed with a nonlinear least-squares routine based on the Levenberg-Marquardt algorithm<sup>29</sup> with unity weighting and double precision arithmetic.

A point density ( $n_{\text{dec}}$ ) of ten points per decade was chosen to sample the frequency-domain data. This sampling density did not affect our ability to approximate the continuum limit to the fitting of one function to the other. This can be demonstrated by comparing the fit parameters for a KWW function with  $k=0.5$  obtained for data with 5, 10, and

20 points per decade. The data were generated over a frequency range of  $1 \times 10^{-4}$  Hz to  $1 \times 10^9$  Hz. The HN  $\alpha$  ( $\beta$ ) exponents obtained for these three point densities (5, 10, and 20 points/decade) were 0.8089 (0.5363), 0.8086 (0.5367), and 0.8084 (0.5369), respectively; the values obtained for  $\chi^2/n_{\text{dec}}$  were  $3.8787 \times 10^{-4}$ ,  $3.8676 \times 10^{-4}$ ,  $3.8618 \times 10^{-4}$ , respectively, where  $\chi^2$  is defined as

$$\chi^2 \equiv \sum_{i=1}^N (y_i - \hat{y}_i)^2. \quad (5)$$

In the above equation,  $y_i$  is the value of the function at a frequency  $f_i$ ,  $\hat{y}_i$  is the value of the model approximating the function at the same frequency, and  $N$  is the number of data points.

### B. Choice of metric

As we pointed out in Paper I, when examining the ability of one function to represent another function, the standard deviation  $\sigma$  is not a good measure, especially for relaxation functions. A relaxation function in the frequency domain evolves from unity to zero for the real component and from zero to a maximum of less than 0.5 and back to zero for the imaginary component over a finite frequency range. Therefore, if a wide enough frequency range is chosen, all relaxation functions will agree to within an arbitrary tolerance. However, the  $L_\infty$  norm (the maximum deviation) is not significantly affected over a sufficiently wide frequency range. We will demonstrate this in the discussion that follows.

Since we are examining the ability of one exact function to approximate another exact function, the standard deviation  $\sigma$  loses any statistical meaning. We stress that we are not fitting to a set of data that can be represented by an exact model plus a random deviate with a sampled population. To emphasize this, henceforth in the paper we will refer to  $\sigma^2$  as the mean-squared deviation rather than as the variance and will define it as

$$\sigma^2 = \frac{\chi^2}{N}. \quad (6)$$

To demonstrate the reason why  $\sigma$  is not a good measure, we consider the mean-squared deviation  $\sigma^2$  of two functions, with  $f(\omega)$  being the larger of the two functions. (For simplicity, we are setting  $\tau=1$  s in the discussion that follows.) The upper bound on  $\sigma^2$  is then given in the continuum limit to be

$$\begin{aligned} \sigma^2 &= \frac{\int_{\omega_1}^{\omega_4} f(\omega)^2 d\omega}{(\omega_4 - \omega_1)} \\ &= \frac{\int_{\omega_1}^{\omega_2} f(\omega)^2 d\omega + \int_{\omega_2}^{\omega_3} f(\omega)^2 d\omega + \int_{\omega_3}^{\omega_4} f(\omega)^2 d\omega}{(\omega_4 - \omega_1)}, \quad (7) \end{aligned}$$

where the three integrals on the right-hand side of Eq. (7) refer to the low-frequency tail, central region of the dispersion peak, and the high-frequency tail. It is clear that the integral for the central region is bounded for a relaxation

process. If we then treat the tails by their limiting power-law behaviors through suitable choices for  $\omega_2$  and  $\omega_3$ , we obtain the following for the low-frequency limit (for  $\gamma > 0$ ,  $\omega_1 < \omega_2 \ll 1$ ):

$$\lim_{\omega_1 \rightarrow 0} \frac{\int_{\omega_1}^{\omega_2} \omega^\gamma d\omega}{(\omega_4 - \omega_1)} = \frac{(\omega_2)^{1+\gamma}}{(\omega_4)(1+\gamma)} \equiv 0, \quad (8)$$

and for the high-frequency limit (for  $\delta > 0$ ,  $\omega_4 > \omega_3 \gg 1$ ):

$$\lim_{\omega_4 \rightarrow \infty} \frac{\int_{\omega_3}^{\omega_4} \omega^{-\delta} d\omega}{(\omega_4 - \omega_1)}, \quad (9)$$

which is given for  $\delta=1$  by

$$\lim_{\omega_4 \rightarrow \infty} \frac{\ln(\omega_4/\omega_3)}{(\omega_4 - \omega_1)} = 0, \quad (10)$$

and for  $\delta \neq 1$  by

$$\lim_{\omega_4 \rightarrow \infty} \frac{(\omega_4)^{1-\delta} - (\omega_3)^{1-\delta}}{(\omega_4 - \omega_1)(1-\delta)} = 0. \quad (11)$$

Therefore, if  $\omega_2$  is chosen to be sufficiently small and  $\omega_3$  is chosen to be sufficiently large so that the power-law approximation is reached and that there is a negligible contribution to the total relaxation, then the upper bound on  $\sigma^2$  is given by

$$\sigma^2 = \frac{\int_{\omega_2}^{\omega_3} f(\omega)^2 d\omega}{(\omega_4 - \omega_1)}. \quad (12)$$

Therefore,  $\sigma^2$  can be made arbitrarily small by the appropriate choice of frequency window. The same conclusion can be applied to the real component by replacing the low-frequency error term in Eq. (8) by  $(1 - \omega^{\gamma/2})^2$ .

The difference between the maximum deviation  $\Delta_{\text{max}}$  (where  $\Delta_{\text{max}} = \sup|f_2 - f_1|$ , with  $f_1$  and  $f_2$  the two functions being compared) and  $\sigma^2$  will be further demonstrated by fitting the HN function to the KWW transformed data over a frequency range sufficient to describe the relaxation, and then increasing the frequency range and refitting the data. It will be shown that the data with the smaller frequency range has approximately the same parameters and the same maximum deviations, however the standard deviation of the increased frequency range is smaller.

## III. RESULTS AND DISCUSSION

### A. Introductory remarks

Following our discussion in Sec. II B as to why  $\Delta_{\text{max}}$  is a better measure than  $\sigma^2$  of how well the KWW function is approximated by the HN function, we consider a fit of the HN equation to the imaginary component of the transformed KWW data for  $k=0.5$  for two different frequency ranges ( $1 \times 10^{-6}$  s $^{-1}$  to  $1 \times 10^8$  s $^{-1}$  and  $1 \times 10^{-4}$  s $^{-1}$  to  $1 \times 10^7$  s $^{-1}$ ). The value for  $\sigma^2$  decreases from  $3.48 \times 10^{-3}$  to  $3.07 \times 10^{-3}$  while  $\Delta_{\text{max}}$  stays constant at a value of 7.47

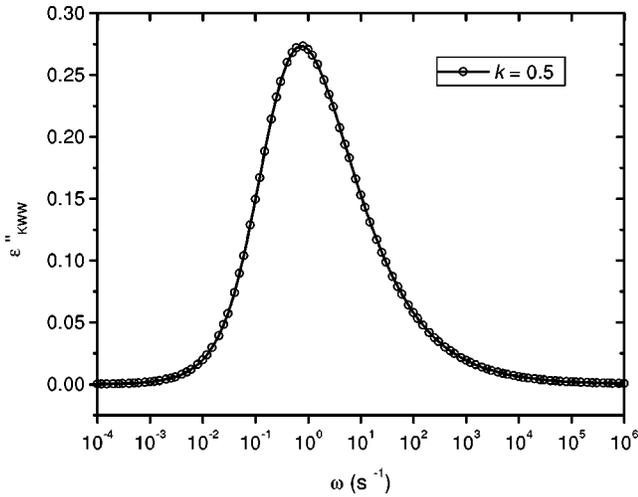


FIG. 1. Plot of imaginary component for the Laplace transformed KWW function with  $k=0.5$ . Note that the line that is shown connecting the data points consists of straight line segments.

$\times 10^{-3}$ , indicating that while  $\sigma^2$  would indicate a better fit,  $\Delta_{\max}$  indicates no change in the “goodness” of fit. As further confirmation of our above discussion  $\chi^2$  is unchanged by the addition of 30 square residuals.

This, and our discussion in Paper I on the inapplicability of statistics to numerical approximations, demonstrates some of the crucial flaws in the analyses performed by Alvarez and co-workers and by Havriliak and Havriliak. Their conclusions regarding the goodness of fit derived from the low values of  $\sigma$ , are incorrect for the reasons we have demonstrated. In the following section, using a properly sensitive measure, we will critically analyze the ability of the HN function to approximate the KWW function.

Before presenting the results from our curve fitting, we wish to make a few comments about the transformed KWW data. In Fig. 1 we have plotted a typical loss curve for the transformed KWW data. To demonstrate the smoothness of the data we have used a straight line interpolator between our data points. It is readily apparent that the data sufficiently describe the function. This is in accord with Ref. 24 where the Cole-Davidson function for  $\beta=0.5$  was compared with the known analytic answer and the maximum error was  $0.5 \times 10^{-6}$  for a specified tolerance of  $1 \times 10^{-6}$ .

Figure 2 is a Cole-Cole plot of the Laplace transform of the KWW functions for values of  $k$  ranging from 0.1 to 1.0. Several things can be observed from this plot. As  $k$  is decreased, the maximum loss is decreased. The characteristic relaxation time is shifted from  $\epsilon'=0.5$  at  $k=1.0$  to  $\epsilon'=0.6$  at  $k=0.1$  (in the plot, we have put a cross where  $\omega\tau$  is equal to unity). The number of decades required to describe the entire relaxation process increases with decreasing exponent (in the plot, we have put a symbol on the curve for every decade). Finally, it should be noted that as  $k$  is decreased from 1.0 to 0.1,  $\omega\tau$  at the loss maximum is shifted from 1.0 to 0.6 Hz. This demonstrates that the use of the method of Alvarez and co-workers<sup>18,19</sup> to perform a time to frequency domain transform is unnecessary because of the stability of our numeric Laplace transform.

**B. Equivalence of the HN and KWW functions**

Table I shows the results of our fits of the HN equation to the transformed KWW data. Our parameters are close to

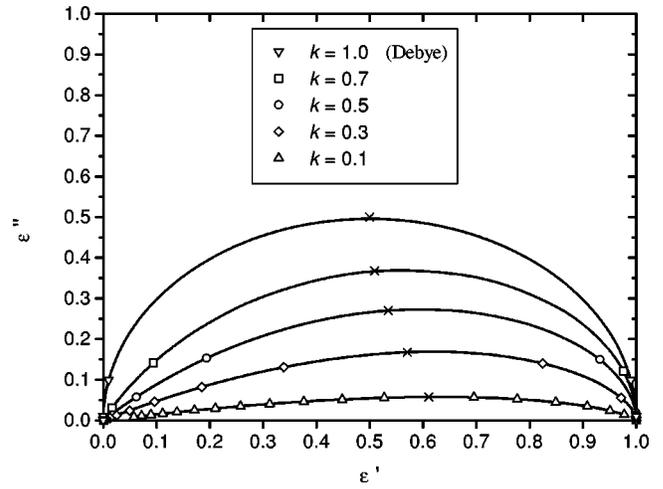


FIG. 2. Cole-Cole plot of the Laplace transformed KWW function for values of  $k=0.1, 0.3, 0.5,$  and  $0.7$ . The symbols on the plot correspond to the beginning of a decade, whereas the line is passed through all 10 points per decade. The cross is placed at  $\omega\tau$  equal to unity.

those of Havriliak and Havriliak<sup>25</sup> except for those obviously in error (in their Table I they have two headings for  $k=1.0$ , both of which are obviously not for  $k=1.0$ ) and agree reasonably well with those of Alvarez and co-workers.<sup>18,19</sup> The differences between the parameters can be attributed to differences in the ways in which the functions were generated, how the sampling density was chosen, and the range of the data. We examined the method of transformation of Havriliak and Havriliak<sup>30</sup> for the KWW function, Cole-Davidson function, and a series of discrete exponentials. In all cases, the Havriliak-Havriliak transform had larger errors on the low-frequency side of the relaxation. This is consistent with the discrepancies observed between our HN parameters and theirs, which is observed in their higher values for  $\alpha$ . None of these discrepancies, however, affect our conclusions.

In Fig. 3, we have plotted the residuals  $\Delta=(\epsilon''_{\text{KWW}}-\epsilon''_{\text{HN}})$  as a function of angular frequency  $\omega$  for the fits to the imaginary portion of the transformed KWW data only (fit

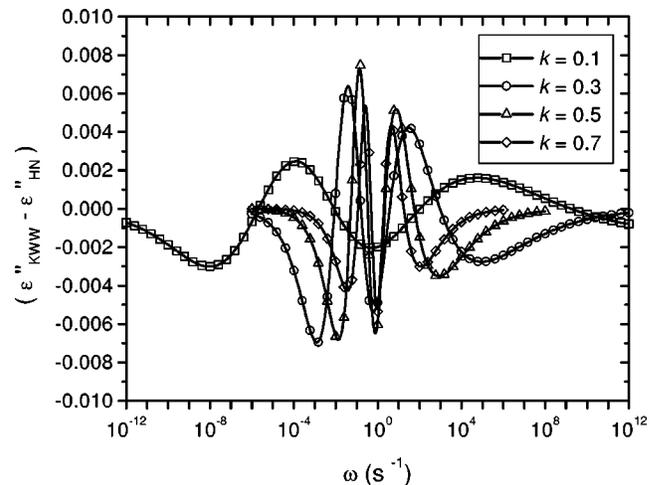


FIG. 3. Residuals  $\Delta=(\epsilon''_{\text{KWW}}-\epsilon''_{\text{HN}})$  as a function of angular frequency for the fits performed to the imaginary component of the Laplace transformed KWW data.

TABLE I. Results of fits to the Laplace transformed KWW data with the Havriliak-Negami equation.

$k$	Frequency range	$\epsilon_\infty$	$(\epsilon_0 - \epsilon_\infty)$	$\alpha$	$\beta$	$\tau$ (s)	$\chi^2$	Fit <sup>a</sup>
0.1	$10^{-12}$ – $10^{29}$ s <sup>-1</sup>	-0.0145	1.03	0.229	0.342	180	$6.63 \times 10^{-4}$	i
		-0.00471	1.02	0.221	0.383	63.8	$7.68 \times 10^{-3}$	ri
0.3	$10^{-6}$ – $10^{12}$ s <sup>-1</sup>	-0.0125	1.03	0.595	0.404	6.46	$1.51 \times 10^{-3}$	i
		-0.00382	1.01	0.594	0.428	5.32	$6.00 \times 10^{-3}$	ri
0.5	$10^{-6}$ – $10^8$ s <sup>-1</sup>	-0.0106	1.02	0.810	0.516	2.73	$1.27 \times 10^{-3}$	i
		-0.00311	1.01	0.816	0.528	2.58	$3.88 \times 10^{-3}$	ri
0.7	$10^{-6}$ – $10^6$ s <sup>-1</sup>	-0.00679	1.01	0.924	0.673	1.68	$5.49 \times 10^{-4}$	i
		-0.00207	1.00	0.929	0.680	1.65	$1.60 \times 10^{-3}$	ri
1.0	$10^{-4}$ – $10^4$ s <sup>-1</sup>	$-2.98 \times 10^{-8}$	1.00	1.000	1.000	1.000	$2.26 \times 10^{-12}$	i
		$5.41 \times 10^{-8}$	1.00	1.000	1.000	1.000	$6.65 \times 10^{-12}$	ri

<sup>a</sup>i indicates a fit to the imaginary component only, while ri indicates a fit to both the real and imaginary components.

A). A similar plot is shown in Fig. 4 for the fits performed simultaneously to the real and imaginary portions of the transformed KWW data (fit B). The summary of these plots can be found in Table II, where we list  $\Delta_{\max}$  for each value of  $k$ . (N.B. For each of the two  $\Delta$  plots, the line is a spline to the data and the symbols are plotted for every fourth data point.) From this data, it is apparent that the lowest value for  $\Delta_{\max}$  is  $3.02 \times 10^{-3}$ , excluding the case where  $k=1$ , for which the HN function has a known analytical solution ( $\alpha=1$  and  $\beta=1$ ). This difference is resolvable by the time domain spectrometer,<sup>22</sup> which has a relative sensitivity of less than  $1 \times 10^{-3}$  of the total dispersion strength, and for commercially available inductance-capacitance-resistance bridges. Therefore, the conclusion of Alvarez and co-workers<sup>18,19</sup> and Havriliak and Havriliak,<sup>25</sup> that under certain circumstances the two functions are indistinguishable, is incorrect.

As a further demonstration of our results, we consider the case of an exponential decay ( $k=1$ ) which is exactly repre-

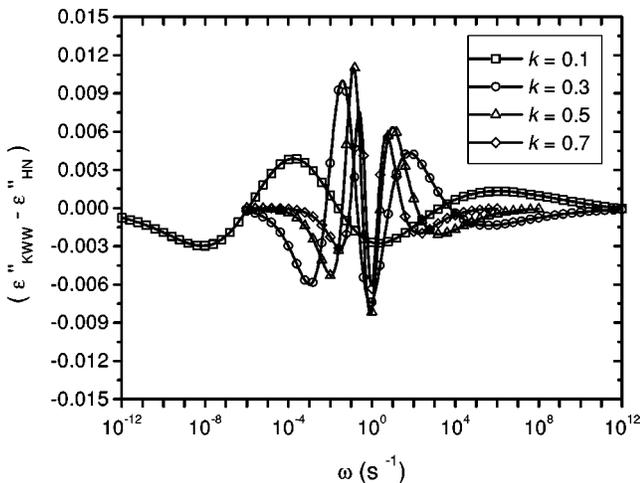


FIG. 4. Residuals  $\Delta = (\epsilon''_{\text{KWW}} - \epsilon''_{\text{HN}})$  as a function of angular frequency for the fits performed simultaneously to the real and imaginary components of the Laplace transformed KWW data.

sented by both the HN and KWW functions (see Tables I and II for the fitting results). In this case, fitting one to the other should give an exact fit, however, there will be significant residuals due to round off errors that will act as a random deviate. Our computed value for  $\sigma^2$ , the mean-squared deviation, is  $2 \times 10^{-7}$  with  $\Delta_{\max} = 5 \times 10^{-7}$ . These are expected values for the truncation error for six digit representations. The computed exponents  $\alpha$  and  $\beta$  are equal to unity as expected.

**C. Limiting power-law behavior**

To examine the ability to determine the limiting exponents, using the method of Paper I, we locally fit the imaginary portion of the transformed KWW function to the following power-law equation as a function of normalized frequency  $x$  ( $x = \omega \tau$ ):

TABLE II. Maximum absolute value of the residual  $|\Delta_{\max}|$  as a function of KWW exponent  $k$ .

$k$	$\omega_{\min}$ (s <sup>-1</sup> )	$\omega_{\max}$ (s <sup>-1</sup> )	$\Delta_{\max}$	$\omega_{\Delta_{\max}}$ (s <sup>-1</sup> )	fit <sup>a</sup>
0.1	$1 \times 10^{-12}$	$1 \times 10^{29}$	$3.02 \times 10^{-3}$	$1.0 \times 10^{-8}$	i
			$3.88 \times 10^{-3}$	$1.5 \times 10^{-4}$	ri
0.3	$1 \times 10^{-6}$	$1 \times 10^{12}$	$6.98 \times 10^{-3}$	$1.2 \times 10^{-3}$	i
			$1.01 \times 10^{-2}$	$4.0 \times 10^{-2}$	ri
0.5	$1 \times 10^{-6}$	$1 \times 10^8$	$7.47 \times 10^{-3}$	0.15	i
			$1.10 \times 10^{-2}$	0.12	ri
0.7	$1 \times 10^{-6}$	$1 \times 10^6$	$5.52 \times 10^{-3}$	0.25	i
			$7.73 \times 10^{-3}$	0.25	ri
1.0	$1 \times 10^{-4}$	$1 \times 10^3$	$4.8 \times 10^{-7}$	0.4	i
			$5.1 \times 10^{-7}$	1.5	ri

<sup>a</sup>i indicates a fit to the imaginary component only, while ri indicates a fit to both the real and imaginary components.

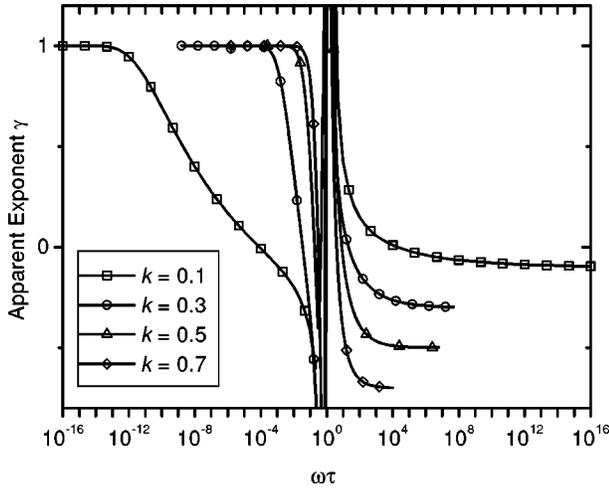


FIG. 5. Apparent exponent  $\gamma$  as a function of normalized frequency.

$$\epsilon''(x) = A + Bx^\gamma, \quad (13)$$

with  $A$  and  $B$  in the above equation being constants. Three points were spaced as a geometric progression with multiplier  $k$ . If Eq. (13) has values of  $x_1$ ,  $x_2$ , and  $x_3$  equal to  $x_1$ ,  $kx_2$ , and  $k^2x_1$ , then the limiting exponent  $\gamma$  can be evaluated as

$$\gamma = \ln \left( \frac{\epsilon''_2 - \epsilon''_3}{\epsilon''_1 - \epsilon''_2} \right) \frac{1}{\ln(k)}, \quad (14)$$

where  $\epsilon''_i$  corresponds to the loss at a normalized frequency  $x_i$ . The results of these fits are shown in Fig. 5. As was expected from asymptotic evaluation of the Fourier transform, the limiting low-frequency exponent was unity for all four values of  $k$  examined and the limiting high-frequency exponent was  $-k$ . Havriliak and Havriliak<sup>25</sup> showed this for the case of  $k=0.5$ .

Several things need to be noted from this. The first, is that since the limiting exponents for the HN equation are  $\alpha$  and  $-\alpha\beta$ , for the low- and high-frequency limits, respectively, for equivalence of the two functions with respect to limiting power-law behavior,  $\alpha=1$  and  $\beta=k$ . For  $k=0.5$  and  $k=0.7$ ,  $\beta$  is close to, but not equal to,  $k$ . For  $k=0.1$  and  $k=0.3$ ,  $\beta$  is very different from  $k$ . Furthermore, in none of the four cases is  $\alpha=1$ . Therefore, it is clear that the two functions are *not equivalent*.

Further important information is obtainable from Fig. 5. Jonscher has postulated a universal dielectric response based on a limiting exponent law.<sup>26,31</sup> From our plot, we can determine how low or high a frequency must be measured for the limiting behavior to be reached. Table III is a listing of this information. It is readily apparent that for  $k=0.1$  the limiting low-frequency power law is unattainable, since a time on the order of  $1 \times 10^5$  y would be required for the low-frequency limit, and the high-frequency limit falls in the ultraviolet region of the spectrum. The other exponents are theoretically attainable with commercially available instruments, or by combinations of several commercially available instruments. However, if both exponents are desired, 11, 9, and 6, decades must be obtainable for  $k=0.3$ , 0.5, and 0.7, respectively.

TABLE III. Approximate high- and low-frequency limits for limiting power-law behavior as a function of the KWW parameter  $k$ .

$k$	Low $\omega\tau$ limit	High $\omega\tau$ limit	Decades
0.1	$1 \times 10^{-14}$	$1 \times 10^{16}$	30
0.3	$1 \times 10^{-4}$	$1 \times 10^7$	11
0.5	$2 \times 10^{-3}$	$1 \times 10^6$	9
0.7	$1 \times 10^{-2}$	$1 \times 10^4$	6

This is unlikely to be achievable under normal experimental conditions. Also, over these required ranges in frequency, it is expected that there will be other relaxations that will appear and “corrupt” the limits of the relaxation process of interest. Therefore, the utility of a universal power law becomes suspect in these cases.

#### D. Implications on theories of relaxation

In the above discussions, we have examined the ability of the HN function to approximate the KWW function without any discussion of the underlying physics. The ability, or inability, of one of these functions to approximate the other’s behavior does not discount their use as interpolating functions; their utility should be considered individually for each case examined. Although theories have been put forth to predict the functional forms of both the KWW and HN functions, the “true” function is uncertain and could lie elsewhere. Furthermore, it should be realized that microscopically based theories which predict one or both of these macroscopic functional forms are not necessarily valid proof of the “correctness” of a given form. The difference between the observable macroscopic relaxation and the local, microscopic relaxation behavior has been the subject of much discussion, starting with Debye<sup>32</sup> and his model for rotational diffusion. A more modern development is that due to Fulton,<sup>33,34</sup> who references much of the early work that went beyond Debye. All of these results indicate that there can be significant differences between the macroscopic and microscopic behavior, at least as comparable to those shown between the KWW and HN functions in this work.

#### IV. CONCLUSIONS

We have demonstrated, contrary to earlier conclusions by Alvarez and co-workers<sup>18,19</sup> and Havriliak and Havriliak,<sup>25</sup> that the KWW and Havriliak-Negami equations are distinctly different functions, which are distinguishable under achievable experimental conditions. It has been shown that the maximum residual  $\Delta_{\max}$  is a far more sensitive measure of the ability of one function to approximate another than  $\sigma$ . Additionally, it has been stressed that it is improper to use a statistical analysis to compare two exact functions; this has not been an analysis of the ability of one function to fit experimental data with a corresponding random deviate.

We would like to point out, however, that the results of this paper were similar to those in Paper I. In that work, we demonstrated that two distinct functions could be made to resemble each other under the appropriate conditions. Clearly, if the experimental data are obtained with uncertain-

ties greater than  $\Delta_{\max}$ , then the two functions will be indistinguishable. However, if the uncertainty is greater than  $\Delta_{\max}$ , then in addition to the difficulties which we mentioned about obtaining the limiting power-law exponents, it is apparent that any values obtained for these exponents will be questionable as the limits of the KWW and HN are quite different. To reiterate a point which we made in Paper I, the final appeal must be made to the measured data and the associated uncertainties. If one of these two functions cannot fit the data, then the issue of the difference between the functions disappears, otherwise extreme care must be taken in comparing the results of the fits and conclusions should be based on proper estimates of the total uncertainty.

The utility of the KWW and HN equations as interpolating functions is not being disputed by this work. However, it should be recalled that both the HN and KWW equations are

empirical functions, and the fact that a given theory reproduces their behavior does not necessarily indicate that the theory is correct, or that these functions are natural laws. As we stated in Sec. III D, a microscopic theory which reproduces these functions may not be valid due to the difference between the microscopic and macroscopic responses.

As a final point, we have shown the stability of our numeric Laplace transform for the KWW function for a wide range of values of  $k$ , and hence the use of the approximations of Alvarez and co-workers and that of Havriliak and Havriliak<sup>30</sup> is unnecessary.

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